

A Mn(IV)-Me₄DTNE complex catalyzed oxidation of lignin model compounds with hydrogen peroxide

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Abstract

1-(3,4-dimethoxyphenyl)ethanol, 1-(3,4-dimethoxyphenyl)-1-propene (mixture of *E*- and *Z*-isomers) and *E*-1,2-diphenyl-ethene were chosen as model compounds to investigate the reactivity of lignin toward hydrogen peroxide catalyzed by [L'Mn(IV)(μ-O)₃Mn(IV)](ClO₄)₂ where L' is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane. All the model compounds investigated were readily oxidized to a significant extent by hydrogen peroxide when catalyzed by this complex. The reaction products were identified by GCMS, and the reaction kinetics was studied. Based on these results, the mechanisms of the reactions have been elucidated. The catalyst preferentially epoxidates C–C double bonds conjugated with aromatic moieties. The activation energy of the reactions was determined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Mn complexes; Catalysis; Hydrogen peroxide; Oxidation; Lignin model compounds

1. Introduction

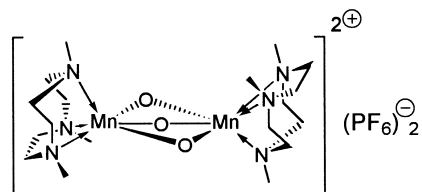
Oxidative degradation of residual lignin in pulp (usually referred as 'pulp bleaching' in the pulp and paper industry) is traditionally accomplished by processes utilizing elemental chlorine and chlorine dioxide. In spite of their excellent selectivity, chlorine and chlorine dioxide are responsible for the formation of a wide variety and a large amount of chloro-organics [1–4], some of which are carcinogenic and mutagenic [5,6]. Under the pressure of the increasing envi-

ronmental demands, bleaching of pulp with inexpensive non-chlorine containing chemicals has been becoming more and more desired. This also facilitates the closure of the bleach plants.

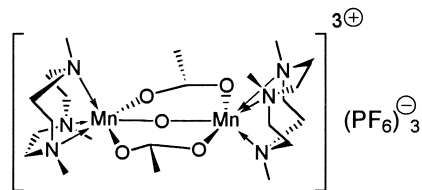
Dioxygen and hydrogen peroxide are among the environmentally benign and widely used alternatives to chlorine and chlorine dioxide by virtue of eliminating the formation of chloro-organics in the bleaching processes. To enhance the removal of lignin without compromising pulp strength, biobleaching processes such as dioxygen–laccase–mediator systems were introduced [7]. Fungal laccase (EC1.10.3.2) is a blue metalloglycoprotein containing four copper atoms in the active sites. The laccase-catalyzed oxidation has been intensively investigated be-

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cause of many interesting characteristics of laccase such as its ability to catalyze the degradation of woods in nature [8] and the usefulness of the laccase-catalyzed oxidation in organic synthesis [9]. Laccase alone, however, is incapable of degrading lignin but promotes its dehydrogenative polymerization [10]. Interestingly, when applied together with a co-substrate or 'mediator', such as 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) [7], laccase is capable of catalyzing oxidation of non-phenolic benzyl alcohols to the corresponding aldehydes as well as to selectively degrade lignin to a significant extent [11,12]. The role of mediators has been intensively studied and has been clarified by our research group [13]. The mediator acts not only as a laccase activator, but also as a co-substrate and an oxidant after undergoing a hydrogen abstraction. However, the commercialization of the laccase–mediator system is not practical at the present time because of the high cost of laccase and the mediators. Mimicking the behaviors of laccase–mediator systems is likely more cost effective and therefore is the highly desired alternative.



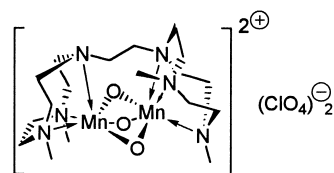
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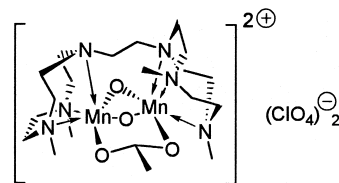
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A group of transition metal complexes has been found to catalyze oxidation of residual

lignin with hydrogen peroxide in the ways similar to those of laccase–mediator systems. A number of papers have been published on the oxidation of alkenes, alkanes [14–18], as well as several electron-rich aromatic compounds [19] with hydrogen peroxide catalyzed by iron and manganese porphyrin-based systems. Hydrogen peroxide has also been used in textile bleaching and its bleaching efficiency has been found significantly improved when catalyzed by a manganese complex [LMn(IV)(μ -O)₃Mn(IV)-L](PF₆)₂ (**1**), as patented in Europe [20], where L is 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃TACN). The catalyst **1** is prepared in situ by oxidation of the precatalyst [LMn(III)(μ -O)(μ -OAc)₂Mn(IV)L](PF₆)₃ (**2**) with hydrogen peroxide in an aqueous solution. Mn-complexes of this class were synthesized in laboratories in the late 1980s [21].



3



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More interestingly, a study was carried out on bleaching of softwood pulps with hydrogen peroxide catalyzed by a complex of this class [L'Mn(IV)(μ -O)₃Mn(IV)](ClO₄)₂ (**3**), where L' is 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (Me₄DTNE). It has been shown on a laboratory scale to be very selective and effective in the degradation of residual lignin without

appreciably affecting the physical properties of the pulps but not the catalyst **1** [22–24]. For a better understanding of the reaction mechanisms involved, we have chosen 1-(3,4-dimethoxy-phenyl)ethanol (**5**), 1-(3,4-dimethoxy-phenyl)-1-propene (**6**) (mixture of *E*- and *Z*-isomers in an approximate molar ratio 85:15), and *E*-1,2-diphenylethene (**7**) as models for non-phenolic lignin structures to investigate the fate of lignin during oxidative degradation with hydrogen peroxide catalyzed by **3**.

2. Results and discussion

The catalyst **3** was produced in situ by oxidation of precatalyst [L'Mn(III)(μ -O)₂(μ -OAc)-Mn(IV)](ClO₄)₂ (**4**) by hydrogen peroxide [20,22]. Two mol equivalents of the precatalyst **4** are oxidized by 1 mol equivalent of hydrogen peroxide to give the catalyst **3** and acetic acid, each in 2 mol equivalents. This process apparently involves nucleophilic substitution of the μ -O-C(CH₃)-O group in the Mn(III) nucleus in the first 1 mol equivalent of **4** by 1 mol equivalent of hydrogen peroxide, followed by transfer of a $3d_{(x^2-y^2)}$ electron from the $e_g(\sigma^*)$ set in the Mn(III) to the -O-O bond of the resulting -Mn(III)-O(H)-OH moiety with concomitant elimination of 1 mol equivalent of hydroxyl radical, and a nucleophilic substitution of the resulting hydroxide anion at the second Mn(VI) nucleus. This results in formation of a Mn(IV)- μ -O-Mn(VI) bond with concomitant elimination of 1 mol equivalent of acetic acid leading to the formation of 1 mol equivalent of **3**. The hydroxyl radical immediately oxidizes the Mn(III) nucleus of a second 1 mol equivalent of **4** to the corresponding Mn(IV) nucleus in a concerted reaction involving a transfer of an electron in the $3d_{(x^2-y^2)}$ orbital of the $e_g(\sigma^*)$ set in the Mn(III) nucleus. This orbital is the highest occupied molecular orbital (HOMO) of the Mn(III) nucleus. The hydroxide group is now bonded to the new Mn(IV) nucleus in the form of a ligand binding, substituting the

Mn(III)-nucleus of the original acetyl ligand binding. A subsequent elimination of a second mole equivalent of acetic acid from this intermediate results in the formation of a second mole equivalent of **3**.

In this study, hydrogen peroxide was found to be incapable of oxidizing **5**, **6**, or **7** when applied alone. Under the catalytic action of **3**, however, these substrates were readily oxidized to a significant extent (Figs. 1–3). Since hydrogen peroxide was used in great excess (molar ratio of H₂O₂/substrate is 100), the reactions are pseudo first order with respect to substrate. The reaction rate constants are listed in the Table 1. The activation energy of the reactions was calculated to be 23.8, 52.9, and 59.1 kJ/mol for the oxidation of **5**, **6**, and **7**, respectively.

The oxidation of **5** with hydrogen peroxide catalyzed by **3** leads mostly to the corresponding α -ketone (**8**) in a yield of approximately 50 mol% within the reaction time of 10 min, almost the same amount as the disappearance of **5** (Scheme 1 and Fig. 1). The substrate **5** also underwent dehydration during the gas chromatographic analysis to give (3,4-dimethoxy-phenyl)ethene (**9**) in an insignificant amount. However, in the case of **6**, 1-(3,4-dimethoxy-phenyl)propane-1,2-epoxide (**10**), 1-(3,4-di-

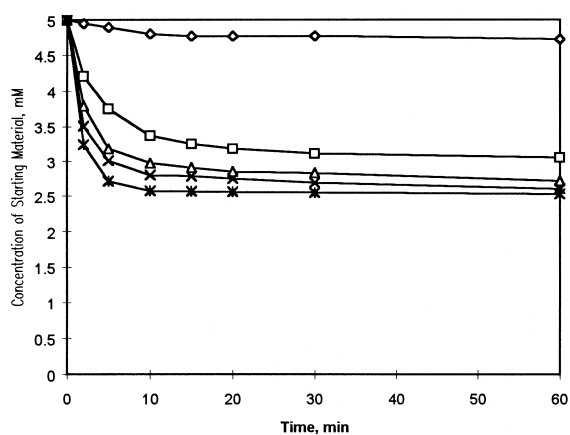


Fig. 1. Disappearance of **5** at various temperatures. $\diamond\diamond\diamond$: uncatalyzed reaction at 50°C; $\square\square\square$: catalyzed reaction at 30°C; $\triangle\triangle\triangle$: catalyzed reaction at 40°C; $\times\times\times$: catalyzed reaction at 50°C; $****$: catalyzed reaction at 60°C.

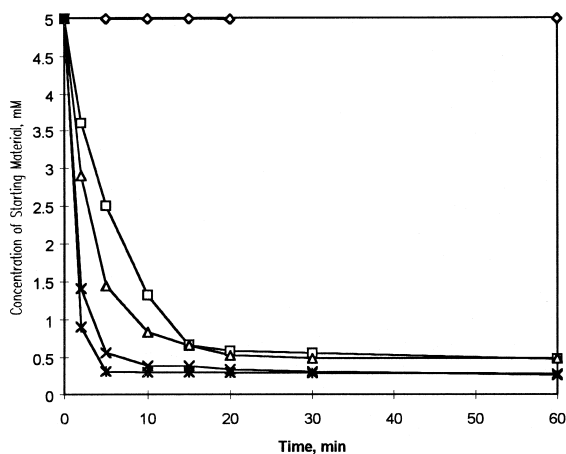


Fig. 2. Disappearance of **6** at various temperatures. $\diamond\diamond\diamond$: uncatalyzed reaction at 50°C; $\square\square\square$: catalyzed reaction at 30°C; $\triangle\square\square$: catalyzed reaction at 40°C; $\times\times\times$: catalyzed reaction at 50°C; $****$: catalyzed reaction at 60°C.

methoxyphenyl)-propane-1,2-diol (**11**), and 3,4-dimethoxybenzaldehyde (**12**) were identified (Scheme 2) as the reaction products. Yields of these products at various reaction times are shown in Table 2. The total yield of these products was approximately 60 mol%, at the reaction time of 10 min, then leveled off. By contrast, the amount of the substrate disappeared was in the range of 90–95 mol% at the reaction time of 10 min, then leveled off (Fig.

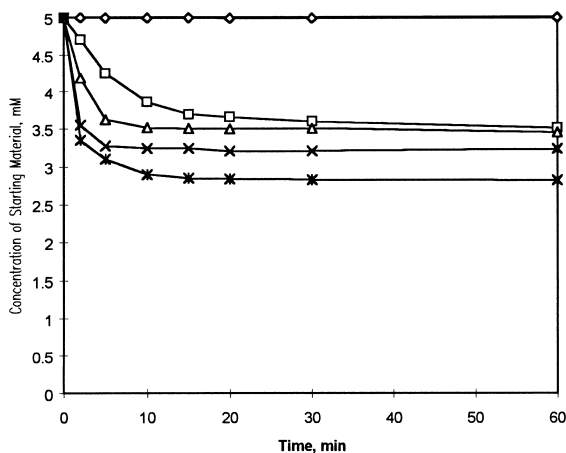


Fig. 3. Disappearance of **7** at various temperatures. $\diamond\diamond\diamond$: uncatalyzed reaction at 50°C; $\square\square\square$: catalyzed reaction at 30°C; $\triangle\square\square$: catalyzed reaction at 40°C; $\times\times\times$: catalyzed reaction at 50°C; $****$: catalyzed reaction at 60°C.

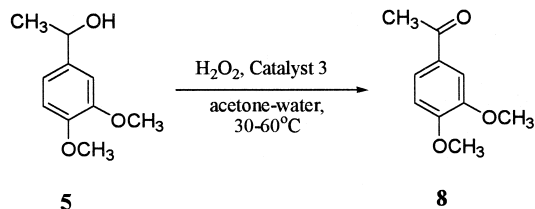
Table 1

Pseudo-first-order reaction rate constants of **5**, **6** and **7** with hydrogen peroxide catalyzed by **3** at various temperatures

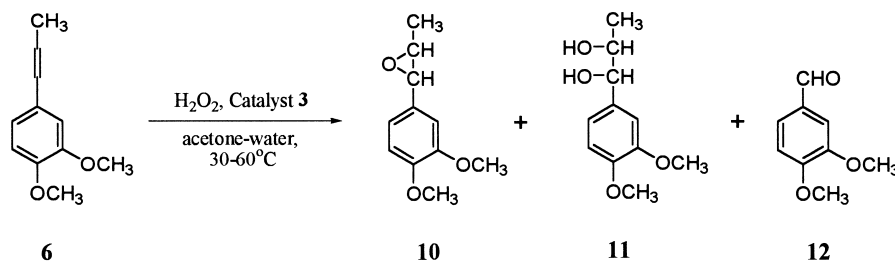
Temperature (°C)	Reaction rate constant (s ⁻¹)		
	5	6	7
30	16.2	10.8	11.8
40	21.0	19.2	28.7
50	29.4	42.0	50.2
60	37.2	70.2	102.5

2). In the case of *E*-1,2-diphenylethene (**7**), *E*-1,2-diphenylethane-1,2-epoxide (**13**) was identified as the major product (Scheme 3). The yield of **13** was approximately 40 mol% at the reaction time of 10 min, then leveled off, which is almost the same as the amount of substrate disappeared (Fig. 3). The fate of unaccounted **5**, **6** and **7** is not known.

Upon initiation of the [L'Mn(IV)(μ-O)₃Mn(IV)]²⁺-catalyzed oxidation (Scheme 2), **6** readily underwent oxidation by hydrogen peroxide to produce **10** in the range of 35–45 mol% within 2 min, the yield of which depends on the reaction temperature. The product then decomposed very quickly to produce **11** and **12**. At 10 min, the yields of **10**, **11**, and **12** were approximately 1.5, 34 and 24 mol%, respectively. The yields of these compounds then leveled off. Nucleophilic attack by H₂O on **9** at C α would produce **11** which would in turn give **12** by further oxidative cleavage of the C α –C β bond. The kinetic data (Table 2) show that catalyst **3** is effective in catalyzing the epoxidation of conjugated double bonds with hydrogen peroxide. However, the data do not reveal whether **12** is produced from **10** via oxidation of **11** in a



Scheme 1. [L'Mn(IV)(μ-O)₃Mn(IV)](ClO₄)₂-catalyzed oxidation of **5** with hydrogen peroxide.

Scheme 2. $[L'Mn(IV)(\mu-O)_3Mn(IV)](ClO_4)_2$ -catalyzed oxidation of **6** with hydrogen peroxide.

consecutive reaction or **11** and **12** are produced from **10** by concurrent reactions. In addition, it is also not clear whether **3** catalyzes oxidation of **10** and **11**. A further investigation is being conducted to clarify the fate of the unaccounted compounds **5**, **6** and **7**, that would in turn lead to elucidation of the reaction mechanism.

As demonstrated by the oxidation of **6** and **7** with hydrogen peroxide catalyzed by $[L'Mn(IV)(\mu-O)_3Mn(IV)]^{2+}$, the oxidation leads mainly to epoxidation of the double bonds conjugated with the aromatic rings. In addition, the $[L'Mn(IV)(\mu-O)_3Mn(IV)]^{2+}$ -catalyzed reactions proceed at fast rates which is highly desired in terms of its potential commercialization. The oxidation is almost complete in 15 min. As shown in the model compound studies, hydrogen peroxide catalyzed by **3** would be capable of oxidizing the α -hydroxyl groups in lignin to their corresponding carbonyl groups which would be susceptible to further nucleophilic attack by hydrogen peroxide anion resulting in further degradation. In addition, the C–C double bonds conjugated with aromatic moieties present in residual lignin would be readily oxidized by hydrogen peroxide catalyzed by **3**,

resulting in bond cleavage leading to the further degradation of lignin via corresponding epoxide intermediates. In order to further understand the oxidative degradation of residual lignin by these processes, residual lignin is being isolated from pine kraft pulps. After purification and characterization, the resulting residual lignin preparation will be treated with hydrogen peroxide catalyzed by the Me_4DTNE type $Mn(IV)$ complex **3** to determine the structural changes of lignin that occur during the treatment.

3. Experimental

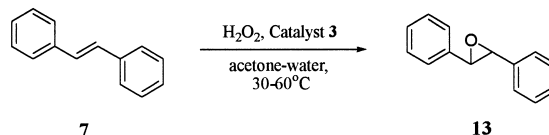
3.1. General procedure for non-catalyzed oxidation

To a solution of 0.05 mmol substrate in 5 ml $(CH_3)_2CO$ were added 0.57 g 30% aqueous solution of H_2O_2 (approximately 5 mmol) and 0.05 mmol 3,4-dichlorotoluene as the internal standard. $(CH_3)_2CO$ was then added to the resulting solution until a total volume is 10 ml. The solution was heated at $50^\circ C$ for 2 h. Samples of the reaction mixture were taken at certain time intervals and extracted with CH_2Cl_2 . The resulting solutions were then dried over

Table 2

Products of oxidation of **6** with hydrogen peroxide catalyzed by **3** at $50^\circ C$ (expressed in yield of products as a function of reaction time)

Reaction time (min)	Yield (%)		
	Epoxide 10	Diol 11	Benzaldehyde 12
2	47.4	1.6	1.5
10	1.5	34.0	24.2
120	1.4	37.9	24.3

Scheme 3. $[L'Mn(IV)(\mu-O)_3Mn(IV)](ClO_4)_2$ -catalyzed oxidation of **7** with hydrogen peroxide.

anhydrous Na_2SO_4 , and analyzed by GC and GCMS.

3.2. General procedure for catalyzed oxidation

To a solution of 0.05 mmol substrate in 5 ml $(\text{CH}_3)_2\text{CO}$ were added 0.57 g 30% aqueous solution of H_2O_2 (approximately 5 mmol) and 0.05 mmol 3,4-dichlorotoluene as the internal standard. $(\text{CH}_3)_2\text{CO}$ was then added to the resulting solution until the total volume is 10 ml. The reaction was initiated by addition of 0.9 mg (0.0012 mmol) precatalyst **4** that was oxidized by H_2O_2 in situ into the catalyst **3**. The reactions were carried out at 30, 40, 50, and 60°C. Samples of the reaction mixture were taken at certain time intervals and extracted with CH_2Cl_2 . The sample solutions were dried over anhydrous Na_2SO_4 , then analyzed by GC and GCMS.

3.3. General procedure for gas chromatography

GC analysis was carried out with HP 5890 Series II gas chromatograph instrument fitted with a HP 5 column (cross-linked 5% diphenyl and 95% dimethyl polysiloxane; 30 m \times 0.25 mm i.d., film thickness 0.25 μm). The samples were injected by the HP automatic injector into the injection port at 200°C. The initial oven temperature was 80°C and was held for 1 min, then raised at a rate of 20°C/min to 200°C and held for another 1 min. The oven temperature was again raised at the rate of 20°C/min to 280°C and held for 1 min. Signals were detected by a FID at the temperature of 240°C.

3.4. General procedure for GCMS

GCMS analysis was carried out with a HP GCD Plus gas chromatography instrument equipped with a HP 5 column (cross-linked 5% diphenyl and 95% dimethyl polysiloxane; 30 m \times 0.25 mm i.d., film thickness 0.25 μm). The samples were injected manually at 200°C. The initial oven temperature was 80°C and was held

for 1 min, then raised at a rate of 20°C/min to 200°C and held for another 1 min. Finally, the oven temperature was raised again at the rate of 20°C/min to 280°C and hold for 1 min. The signals were detected by an EID at 240°C.

3.5. Compounds identified by GCMS analysis

3.5.1. Internal standard

3,4-dichlorotoluene: GC-retention time, 4.4 min; eims, m/z (rel. int.), 164 ($\text{M} + 4^+$, 4.3), 162 ($\text{M} + 2^+$, 26.1), 160 (M^+ , 41.3), 127 (32.6), 125 (100).

3.5.2. Compounds identified in the oxidation mixture of 1-(3,4-dimethoxyphenyl)-ethanol (**5**)

(3,4-Dimethoxyphenyl)ethylene (9): GC-retention time, 5.9 min; eims, m/z (rel. int.), 164 (M^+ , 100), 149 (36.2), 121 (14.9), 103 (23.4), 91 (38.3), 77 (31.9).

1-(3,4-Dimethoxyphenyl)ethanol (5): GC-retention time, 7.0 min; eims, m/z (rel. int.), 182 (M^+ , 61.7), 167 (91.5), 139 (100), 124 (29.8), 108 (18.1), 91 (6.4), 77 (16.0).

3,4-Dimethoxyacetophenone (8): GC-retention time, 7.3 min; eims, m/z (rel. int.), 180 (M^+ , 45.7), 165 (100), 137 (10.6), 122 (7.4), 107 (4.3), 79 (11.7).

3.5.3. Compounds identified in the oxidation mixture of 1-(3,4-dimethoxyphenyl)-1-propene (**6**)

3,4-Dimethoxybenzaldehyde (12): GC-retention time, 6.7 min; eims, m/z (rel. int.), 166 (M^+ , 100), 151 (10.6), 137 (4.3), 95 (31.9), 77 (27.7), 165 (59.6).

1-(3,4-Dimethoxyphenyl)-1-propene (6): GC-retention time, 6.8 min; eims, m/z (rel. int.), 178 (M^+ , 100), 163 (36.2), 147 (10.6), 115 (12.8), 107 (37.2), 91 (31.9), 77 (14.9).

1-(3,4-Dimethoxyphenyl)propane-1,2-epoxide (10): GC-retention time, 7.3 min; eims, m/z (rel. int.), 194 (M^+ , 16.0), 151 (100), 135 (3.2), 107 (10.6).

1-(3,4-Dimethoxyphenyl)propane-1,2-diol (11): GC-retention time, 8.7 min; eims, m/z

(rel. int.) 212 (M^+ , 7.4), 178 (2.1), 167 (100), 151 (6.4), 139 (63.8), 124 (21.3), 108 (14.9).

3.5.4. Compounds identified in the oxidation mixture of *E*-1,2-diphenylethene (7)

E-1,2-Diphenylethene (7): GC-retention time, 8.3 min; eims, m/z (rel. int.) 180 (M^+ , 100), 179 (97.9), 178 (61.7), 165 (48.9), 152 (12.8), 89 (23.4), 76 (14.9).

E-1,2-Diphenylethane-1,2-epoxide (13): GC-retention time, 8.4 min; eims, m/z (rel. int.) 196 (M^+ , 46.8), 195 (48.9), 178 (18.1), 167 (100), 152 (19.1), 105 (19.1), 90 (76.6), 89 (87.2).

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